The Alloying Behaviour of Gold

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Our knowledge of the alloying characteristics of gold is now extensive, much of it conforming to the general theory of alloying developed over the past few decades. In the first part of this review the formation of solid solutions is described in terms of atomic structure. In the second part the factors affecting the formation of compounds of gold with other metals will be considered.

Part I SOLID SOLUTIONS

Gold is a member of Group 1B of the Periodic Table and is the densest of the three metals copper, silver and gold. It owes its unique position as a coinage and jewellery material to its relative inertness towards common corrosive components of the environment, though compounds with carbon (Au_2C_2) and oxygen (Au_3O_2) are known. In much of its chemistry and metallurgy gold is similar to copper and silver, owing essentially to the similar electronic constitutions of the three metals. Considering first the free atoms, in each case the n electrons which balance the nuclear charge are arranged in groups of increasing energy such that (n—1) are in chemically unreactive 'closed shells' of which the outermost are, in quantum number terminology, the 3d, 4d and 5d groups for copper, silver and gold respectively. These (n—1) electrons plus the nucleus form the ion. The nth electron has an energy higher than that of the outermost complete group and is known as the valency electron (the 6s electron in the case of gold), which can be ionised and take part in chemical reactions. In the solid, the d and s electrons occupy bands of energy states, which overlap as illustrated in Figure 1; the energy of the full d band lies below the highest energy in the s band. In relation to the theory of alloying, copper, silver and gold all behave as essentially monovalent metals, contributing one electron per atom to the s band, though suggestions have been made that further ionisation is possible for gold.

Gold crystallises, like copper and silver, in the face-centred cubic structure (Figure 2). The lattice spacing "a" is 4.078 Å (corresponding values for copper and silver are respectively 3.614 and 4.085 Å); the corresponding value of the closest distance of approach of atoms (2.884 Å) is important in relation to those for other metals in discussing alloy formation. Alloy formation is also influenced by the valencies of the component metals, and correlations between the

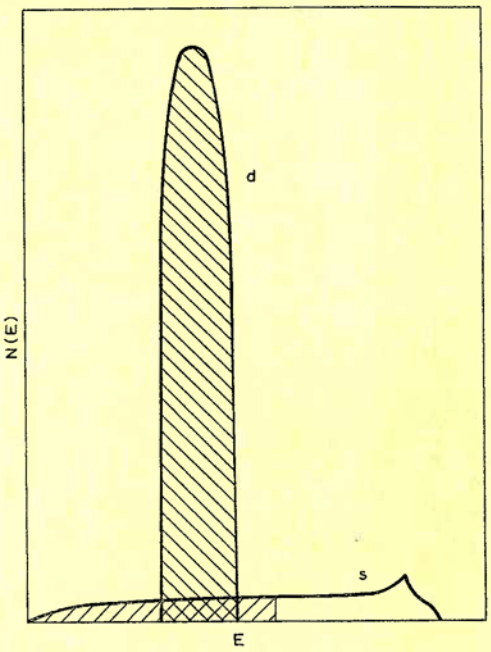

Fig. 1 Overlapping d and s bands for a metal of Group 1B (schematic)

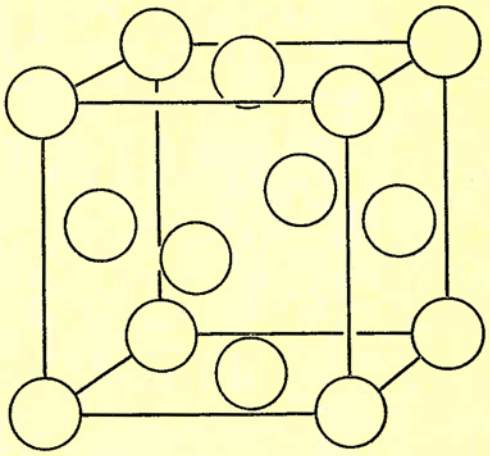

Fig. 2 The face-centred cubic structure

number of valency electrons per atom (e/a) and the solid solubilities of B sub-group metals in the noble metals are of great importance. Correlations also exist between solute valency and the structure and composition of intermediate phases. Thus it was shown by Hume-Rothery, Mabbott and Channel-Evans (1) that the maximum solid solubilities of B sub-group metals in copper, silver and gold corresponded approximately with an e/a value of 1.4. It was later shown that phases with identical or similar crystal structures tended to occur at e/a values of 3/2, 21/13 and 7/4. Further reference will be made to these phenomena in later sections. It may be noted here, however, that for many years it was thought that these regularities were explicable in terms of the electron theory of metals, according to which the variation of the number of electronic energy states per unit energy range in the conduction band of a solid metal depends intimately on the spatial geometry of the crystal structure. The graph of density against energy takes a form like that of Figure 3, and according to the earlier theories the number of electrons per atom in copper corresponded to filling this distribution to the limit of the shaded area. Solution of a polyvalent solute increases the occupied area and it was suggested that the process could continue until the peak of the curve was reached; thereafter a small increase in the number of electrons per atom was thought to cause a relatively large energy increase leading to instability with regard to other possible structures. The peak of the curve, according to the earlier theories, corresponded excellently to the presence of 1.4 electrons per atom.

Modern experimental work which allows a closer definition of the form of the density of states curve is at variance with this, and suggests strongly that the curve is of such a form that the peak has been reached

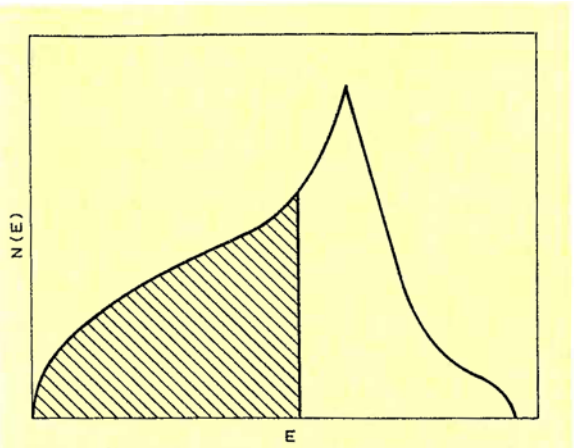

Fig. 3 N(E)/E curve characteristic of copper, silver or gold according to earlier theoretical interpretations

in the pure metal at 1 electron per atom (2). Doubt is therefore thrown upon the simple theoretical interpretation. Various attempts, beyond the scope of this review, have been made to reconcile modern experimental work with the earlier empirical systematisation (3). These embody the suggestion that the form of the valency band is altered by the solution process (3) but the details are complex and the position uncertain. Empirically, however, it may be accepted that the maximum solid solubilities of the B sub-group metals in the noble metals tend to occur at an e/a ratio of 1.4, while phases of characteristic structure occur at ratios of 3/2, 21/13 and 7/4 electrons per atom.

Solid Solution Formation in Gold

At an early stage in the development of alloy theory Hume-Rothery, Mabbott and Channel-Evans showed (1) that the relative sizes of the atoms of the

Table I

Solutes of Favourable Size Factor with Respect to Gold

Group of Periodic Table

Period		1A	2A	3A	4A	5A	6A	7A	8			1B	2B	3B	4B	5B	6B	
1st Short		Li																
2nd Short			Mg	Al														
1st Long				Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As		
2nd Long					Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb		
3rd Long					Hf	Ta	W	Re	Os	Ir	Pt		Hg			Bi	Te	

Table II

Solid Solubilities in Gold of Elements of Unfavourable Size Factor

Group of Periodic Table	Solute	Maximum Solubility At.% Solute	Temperature °C	Group of Periodic Table	Solute	Maximum Solubility At.% Solute	Temperature °C
1A	Na	extremely small	—	6B	S	negligible	—
	K	negligible	—		Se	,,	—
	Rb	,,	—		Po	**	—
	Cs	,,	—	Rare Earth	Ce	<0.2	—
2A	Be	much <1	—		Pr	0.55	—
	Ca	negligible	—		Nd	<0.2	—
	Sr	,,	—		Sm	<0.3	780
	Ba	—	—		Gd	0.6	780
3A	La	<0.2	—		Tb	1.0	780
3B	Tl	0.9	800*		Dy	2.1	780
4A	Th	negligible	—		Ho	3.6	778
4B	Si	negligible	—		Er	5.3	—
	Ge†	3.2	356		Tm	6.0	780
	Pb	0.1	700–950		Lu	6.5	780

*Retrograde solubility curve; solubility <131°C (eutectic temperature) is very small and <0.17 at.%[4].
†Borderline size factor.
**In this case, gold exposed to Po vapour gives an indication of solid solution formation but no details are available (5).

component metals of an alloy were of considerable importance. If the atomic diameter of the solute differs from that of the solvent by more than 15 per cent of that of the latter, primary solid solution formation tends to be limited; if the atomic diameter difference lies within this critical limit, extensive solid solution formation is possible provided that other factors, discussed below, are also favourable. As a measure of atomic diameter the closest distance of approach of atoms in the crystal of the element was chosen; though this choice is arbitrary, experience shows that it enables closer correlations between the structures of alloys and atomic sizes than other possible choices. This "size factor" principle, proposed initially for solid solutions in copper and silver, has been shown to apply to alloy formation in a number of solvent metals. In the case of systems with gold as solvent for which sufficient information on the relevant equilibrium diagrams exists, the solutes of favourable size factor are as shown in Table I. The size factor of germanium with respect to gold is borderline, while those for antimony, bismuth and tellurium are subject to some ambiguity. These elements crystallise in structures for which one distance of atomic approach is much shorter than the other and the size factor is favourable if the shorter distance is adopted, but unfavourable considering the longer distance. The distances of approach of atoms are as follows: Sb, 2.904 and 3.364 Å; Bi, 3.111 and 3.481 Å; Te, 2.864 and 3.468 Å.

Elements with unfavourable size factors include the alkali and alkaline earth elements except for lithium and magnesium, and metals of group 3A apart from aluminium and scandium. Rare earth metals (cerium to lutetium in the Periodic Table) are also of unfavourable size factor with respect to gold. Maximum solid solubilities in gold of elements with unfavourable size factors are summarised in Table II and are in all cases small. For other than rare earth metal solutes the highest solubility is 3.2 atomic per cent germanium at 356°C; as already noted, the size factor for germanium is on the borderline of the favourable zone. A maximum of 0.9 atomic per cent thallium dissolves in solid gold at 800°C and it is interesting to note that at this temperature the solid solution is in equilibrium with the liquid alloy. At 131°C, the temperature of the liq→(Au)+(Tl)* eutectic the solubility is less than 0.17 atomic per cent (4). Other analogous cases are known (e.g., the systems Au-In and Au-Sb). For

*A chemical symbol in brackets denotes the solid solution in the metal for which the symbol is enclosed.

rare earth elements the maximum solubility is that for lutetium (6.5 atomic per cent at 780°C); in general the larger solubilities occur for the heavier rare earths since for these metals (except ytterbium) the size factors become slightly less unfavourable with respect to gold than for the lighter rare earth metals.

Reference has already been made to the elements of groups 5B and 6B for which the shorter and longer distances of approach of atoms differ widely. Arsenic is formally of favourable size factor since both distances are within the limits $d_{Au} \pm 0.15\ d_{Au}$; the maximum solubility is, however, only 0.2 atomic per cent at 611°C. For antimony, bismuth and tellurium only the shorter interatomic distances fall within the favourable zone. The solid solubility curve for antimony is of the retrograde type and the solubility reaches a maximum of 1.12 atomic per cent at 600°C, but those of bismuth and tellurium are negligible. Elements of unfavourable size factor, and the electronegative elements of groups 5B and 6B, thus dissolve to limited extents, in agreement with general principles.

The elements of favourable size factor (Table I) show diverse behaviour in that the alloying characteristics of solute metals from the B and A subgroups differ; magnesium and aluminium show similarities to solutes from the B sub-groups. Table III summarises the maximum solubilities in gold of B sub-group elements of favourable size factor. Since elements of the same valency and crystal structure for which the size factors are favourable tend to form complete series of solid solutions, it is not unexpected that copper and silver are completely miscible with gold, though in the Cu-Au system ordered structures are formed at the compositions Cu_3Au, CuAu and $CuAu_3$ (6). With regard to the general principle that maximum solid solubilities of B sub-group metals in the noble metals tend to correspond to e/a=1.4, the situation for gold is clear from Table III. The highest e/a value reached is 1.345 (Au-Cd), as compared with the value of 1.42 for the Ag-Cd system, in which atomic size relationships are very similar. Similar differentials exist on comparing each relevant gold-rich system with the corresponding silver-rich system, and though the electronic factor is clearly operative, causing solubilities to decrease systematically as the solute valency increases, the maximum e/a values reached are approximately 0.1 units below those for the corresponding silver-rich systems. These observations have led to speculations that in its alloys gold may exert a valency exceeding unity. More recently, explanations in terms of alteration, by the inclusion of the solute, of the precise form of the curve of density of states against energy for the valency electron band have been advanced (3) and the position is unclear. It is of interest to note that germanium, of borderline size factor with respect to gold, dissolves only up to an e/a value of 1.096 whereas tin, of favourable size factor achieves a value of 1.206.

Maximum solubilities in gold for solutes of favourable size factor from the A sub-groups are

Table III

Solid Solubilities in Gold of B Sub-group Elements of Favourable Size Factor

Group of Periodic Table	Solute	Maximum Solubility At.% Solute	Electron:Atom Ratio	Temperature °C	Electron Compounds		
					3/2	21/13	7/4
1B	Cu	100*	—	—	—	—	—
	Ag	100	—	—	—	—	—
2B	Zn	31	1.31	404–642	β^1 AuZn	γ_1 Au_5Zn_8	ε $AuZn_3$
	Cd	34.5	1.345	627	β^1 AuCd	γ Au_5Cd_8	ε $AuCd_3$
	Hg	19.1	1.191	416	—	—	—
3B	Ga	12.5	1.25	455	β Au_3Ga	γ Au_7Ga_3†	—
	In**	13.0	1.30	700	ζ Au_3In	γ Au_9In_4	—
4B	Ge‡	3.2	1.096	356	—	—	—
	Sn	6.85	1.206	498	ζ Au_5Sn	—	ε Au_3Sn
5B	Sb	1.12	1.045	600	—	—	—

*Ordered structures are formed at the lower temperatures at compositions Cu_3Au, CuAu and $CuAu_3$.
†Though the composition of this phase does not correspond with 21/13 electrons per atom, it is treated as a displaced γ-structure by Hume-Rothery, Betterton and Reynolds (9).
**The solubility curve is of the retrograde type; at 700°C the primary solid solution is in equilibrium with the liquid.
‡Borderline size factor.

summarised in Table IV. The largest values are shown by vanadium and chromium. Lithium dissolves up to 40 atomic per cent though below 650°C complex structures are formed from the solid solution. The maximum e/a values reached for the solutions in gold of magnesium and aluminium are comparable with those for divalent and trivalent B sub-group metals, and the two short period elements may be classified with them. Assignment of e/a values to the solubilities of elements of groups 4A, 5A and 6A is difficult, owing to uncertainty about the electronic constitutions of these solutes. If valencies of 4, 5 and 6 are allotted to solutes from groups 4A, 5A and 6A respectively, the values in brackets in Table IV are obtained, and there is no tendency to establish a near constant e/a value.

Table IV

Solid Solubilities in Gold of A Sub-group Elements of Favourable Size Factor

Group of Periodic Table	Solute	Maximum Solubility At.% Solute	Electron: Atom Ratio	Temperature °C
1A	Li	40*	1.0	631
2A	Mg	25†	1.25	827
3A	Al	16†	1.32	545
	Sc	6.3	1.13	780
4A	Ti	13	(1.39)	1123
	Zr	7.25	(1.218)	1065
	Hf	negligible	—	—
5A	V	59	(3.36)	1400
	Nb	no information	—	—
	Ta	11.3	(1.45)	1000
6A	Cr	49.7	(3.48)	1160
	Mo	1.25	(1.06)	1054
	W	no information	—	—
7A	Mn	30.8**	—	960
	Re	~0.1	—	1000
	Tc	no information	—	—
8a	Fe	75	—	1168
	Ru	<0.5	—	—
	Os	negligible	—	—
8b	Co	23.5	—	996
	Rh	0.56	—	900
	Ir	no information	—	—
8c	Ni	100‡	—	—
	Pd	100	—	—
	Pt	100‡	—	—
Actinides	U	0.6	—	885

*Below 650°C the solid solution breaks down into complex structures.

†The Au-Mg system contains a 3/2 electron compound AuMg with the β^1 structure. In the Au-Al system there is also a 3/2 electron compound Au_3Al which is of the β type at high temperatures and the μ type at lower temperatures. The system also contains a distorted γ-brass 21/13 electron compound, and an ε phase (c.p. hex) at Au_5Al_3.

**The system contains an apparent β-phase at the composition AuMn.

‡The solid solutions stable at high temperatures in these systems split up on cooling into two separate compositions so that a wide miscibility gap exists between alloys of the same structures but different compositions and lattice spacings.

Tables III and IV indicate that the theoretical principles which apply to solid solution formation in the noble metals apply also to gold. In addition, the formation of complete series of solid solutions (at temperatures above critical limits) between gold and nickel, palladium and platinum is of great interest. These elements are the terminal members of their respective transitional series; in each case the d band is nearly full (9.4 electrons per atom) and the s band contains 0.6 electrons per atom, as compared with a full 5d band (10 electrons per atom) and one 6s electron for gold. Complete solution formation at the higher temperature may thus be understood in terms of similar electronic constitutions. Below certain critical temperatures the Au-Ni and Au-Pt solid solutions break up into two phases, and the boundaries of the miscibility gap are strongly temperature dependent (Figure 4). A further point of interest is that for solutes from groups 4A to 8,

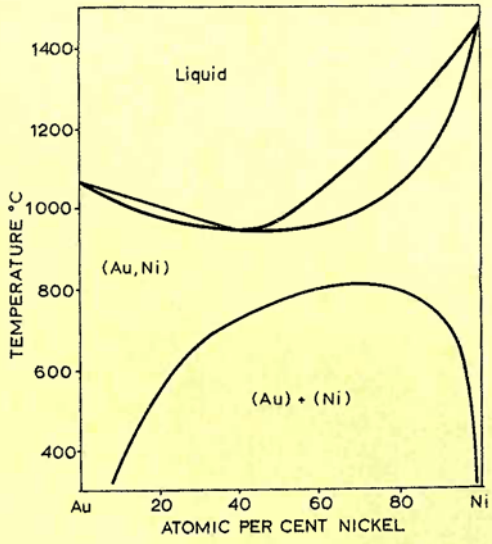

Fig. 4 Equilibrium diagram for the Au-Ni alloys

the first long period elements exhibit the greater solubilities in gold. This conforms with the general theory of alloy formation in which bonding in the body-centred cubic metals of groups 4A to 6A in the second and third long periods is ascribed to a progressively increasing use of directed bonds involving a high contribution from the d electrons (7). Thereafter the participation of d orbitals in the bonding decreases with increasing atomic number in each period.

Solid solution formation between such a body-centred cubic metal and a noble metal, where bonding is chiefly due to s electrons, is difficult, and it is this tendency which accounts for low solubilities of zirconium, molybdenum and tantalum. It is well known that the alloying behaviour of solute metals of the first long period does not conform exactly with that of metals of the other long periods. The partially directed d bonding builds up less rapidly in the first long period, and the relatively high solubilities of vanadium and chromium in gold are a reflection of this. In particular, high solid solubilities are permitted for iron and cobalt, in which the degree of d bonding is less than in the metals of groups 4A to 6A.

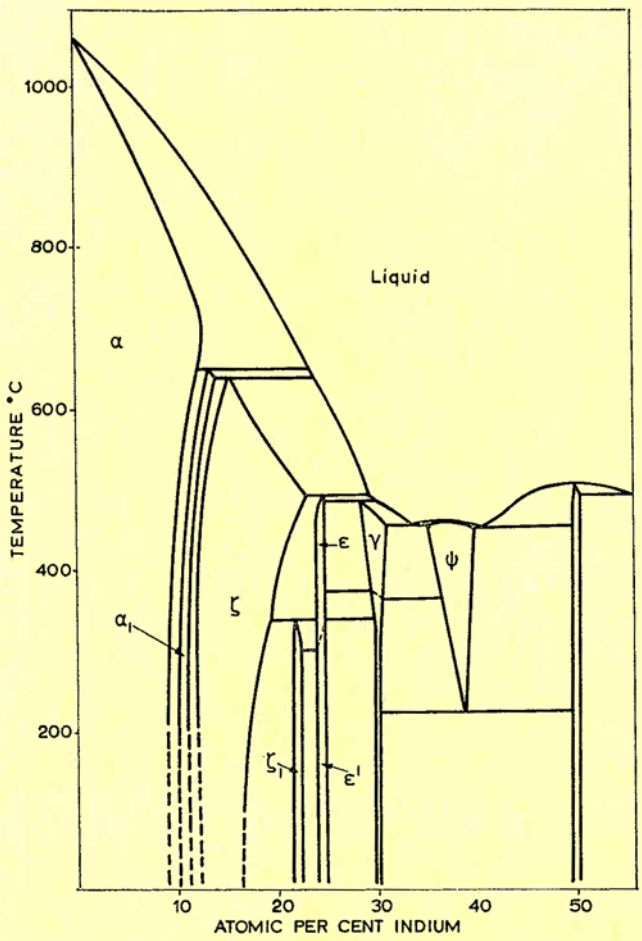

Fig. 5 Equilibrium diagram for the Au-In alloys

The solid solutions of the B sub-group metals, therefore, conform to the theory of alloying which emphasises the contribution made by the e/a ratio. The solid solutions in gold of the A sub-group metals follow no such regular pattern, though the behaviour of nickel, palladium and platinum is easily understood. For the remainder, the precise nature of the bonding in the separate components appears important; differences in the electronic constitutions of gold and the solutes of groups 4A to 6A tend to limit solid solution formation in the relevant systems (except for first long period solutes).

A phenomenon which appears characteristic of gold alloys with B sub-group metals, and which is not in general observed in the alloys of copper and silver, is the intervention of distinct phase structures between the face-centred cubic gold-rich solid solution and the body-centred cubic or close-packed

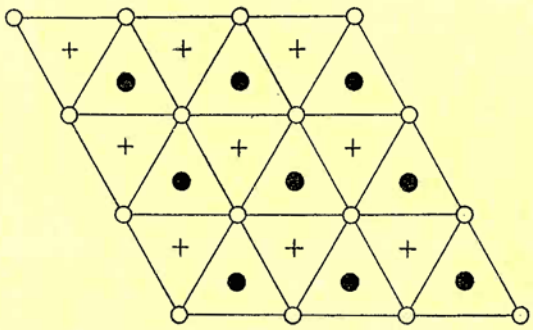

Fig. 6 The disposition of close-packed layers in face-centred cubic and hexagonal close-packed structures. The positions of atoms in A layer, ○; in B layer, +; in C layer, ●

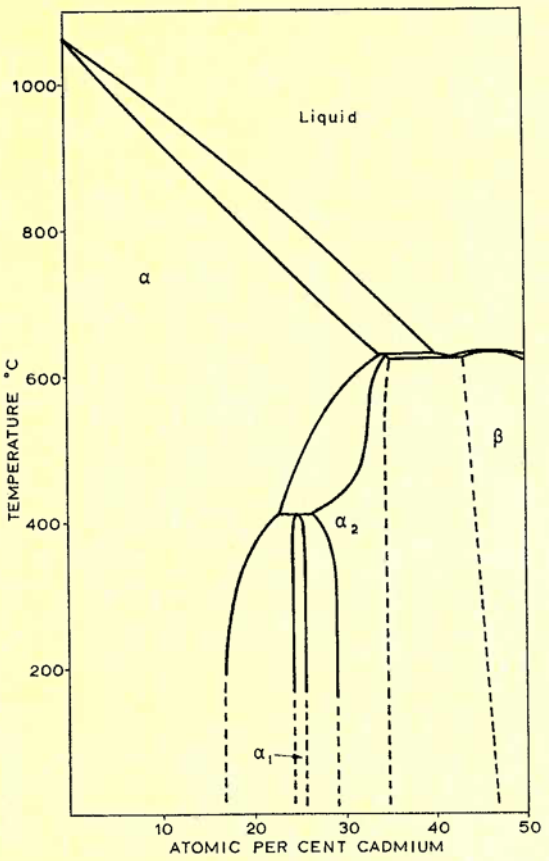

Fig. 7 Equilibrium diagram for the Au-Cd alloys

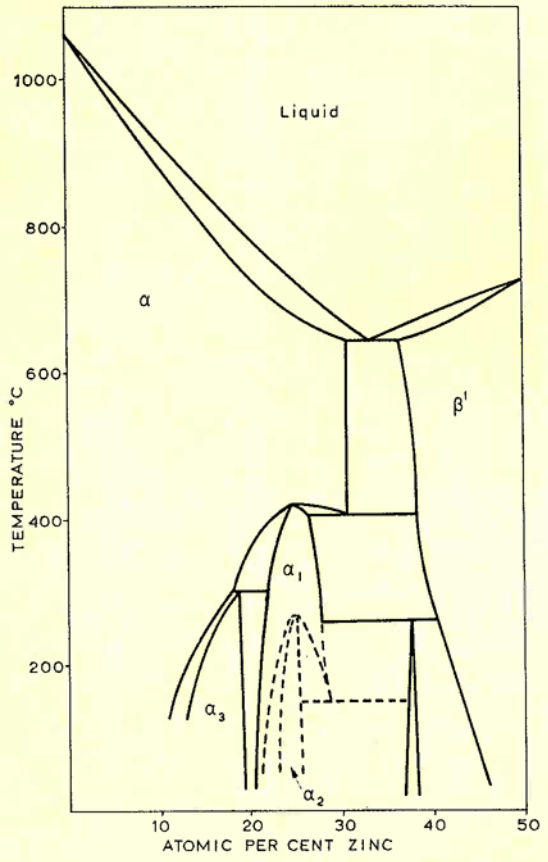

Fig. 8 Equilibrium diagram for the Au-Zn alloys

hexagonal 3/2 electron compound. Where this occurs the equilibrium diagram can take various forms. In the Au-In case (Figure 5) an α_1 phase field occurs between α and ζ; α, is formed peritectically from α+ liquid at 649.25°C (8) so that equilibrium between α and ζ is prevented at all temperatures. It is of great interest to note that α_1 has a hexagonal structure identical with that of neodymium.

The structure of gold is equivalent to a hexagonal structure formed by placing the close-packed {111} plane of the cubic structure horizontal. With such a plane as the base (A layer), the next close-packed layer can be placed with atoms over the centres of alternate triangles as shown by the crosses in Figure 6 (B layer). The next layer can have atoms vertically above those of the A layer, or in positions marked by black circles (C layer). The sequence ABCABC defines the face-centred cubic structure and the sequence ABAB represents the close-packed hexagonal structure. The Au-In α_1 phase has the sequence ABAC of close-packed planes, and so can be regarded as a structural intermediate between α and ζ. Au-Cd alloys (9) are more complicated (Figure 7). Again a hexagonal phase α_2, the structure of which is in doubt, prevents equilibrium between α and β^1. At 412°C α and α_2 react to form α_1 (Au_3Cd); α_1 is a slightly tetragonally distorted ordered structure derived from the face-centred cubic structure. The Au-Zn system (10) is still more complex though α/β^1 equilibrium is possible above 404°C. As shown in Figure 8, α_1 (Au_3Zn) forms congruently at 420°C from α, while at approximately 260°C α_2 forms congruently from α_1. In addition, at 300°C $\alpha+\alpha_1 \rightarrow \alpha_3$ (Au_4Zn). The structures of α_1, α_2 and α_3 appear to be variously deformed and ordered variants of the face-centred cubic structure, as in the cases mentioned above. Further work is needed to explore the factors influencing the formation of these structures. (Complex diagrams in the gold-rich regions are also found in the Au-Mn, Au-V, and Au-Li systems, but the effects appear to bear little resemblance to those discussed above.)

Some factor appears to be operative which is less important in copper and silver alloys. The comparative simplicity of gold-rich Au-In alloys as compared with the Au-Zn and Au-Cd systems derives

from the fact that in the latter cases the extent of the homogeneity range includes compositions such as Au_3X and Au_2X which are important for the formation of long range ordered structures, while the theoretical maximum for a trivalent solute is only 20 atomic per cent.

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The second part of Professor Raynor's review, dealing with the formation of compounds of gold with other metals, will be published in the April issue of Gold Bulletin.

Gold Concentration by Flotation

Reference was made recently to improvements to standard gold extraction processes on the Witwatersrand associated with the recovery or concentration of uranium or pyrite (*Gold Bulletin*, 1975, **8**, (3), 85). A further development of this type was described by S. K. de Kok at a symposium organised by the South African Institute of Mining and Metallurgy in September last year.

The Anglo-Transvaal Consolidated Investment Company recovers pyrite on a large scale from its gold ores by flotation before cyanide treatment. The gold associated with the pyrite is recovered from the concentrate by cyaniding in a separate circuit, and this has resulted in a marked decrease in overall residue values at much coarser grinds than were previously possible. In the course of the development work on the pyrite flotation, it was observed that using a frother plus a dithiophosphate at high pHs, and in the absence of xanthates and activators such as copper sulphate, a high proportion (65 to 75 per cent) of the gold in the ore floated selectively in a concentrate constituting only about 2 per cent of the weight of the feed.

This selective separation of gold from pyrite is now being applied in the cleaning up of gravity concentrates on two mines of the Group. Flotation concentrates directly suitable for smelting are obtained, and amalgamation and retorting have been dispensed with.

The author concludes that flotation is destined to play a larger role in future recovery of gold. Its application to gravity concentrates is immediately attractive, since the bulk of the gold can be collected in these concentrates, without recourse to fine grinding, and the low grade fraction containing probably 10 to 20 per cent of the gold in about 90 per cent of the original ore treated with cyanide, with savings in both capital and working costs. Its application as the primary means of removing gold from the pulp still presents problems, however, since experience has shown that reagents so far found effective in floating gold tend to inhibit cyanidation, so that gold recovery from flotation tailings is more difficult.

Gold being floated from a gravity concentrate in a laboratory flotation cell at the Village Main Reef Gold Mining Company (1934) Limited in Johannesburg, using a frother and a flotation agent containing dithiophosphates. The flotation concentrate is smelted directly so that amalgamation and retorting are eliminated

Photograph by J. Taylor